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THE RAMAN SPECTRUM OF HEXAMETHYLENE-TETRAMINE

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

Hexamethylene-tetramine is one of the few organic substances crystallising in the cubic system. Though its molecules contain as many as 22 atoms, they possess tetrahedral symmetry. The study of the Raman spectrum is therefore of exceptional interest. The substance has been previously investigated by Krishnamurthi (1931); and Kahovec, Kohlrausch, Reitz and Wagner (1938). The polarisation of the Raman lines has, however, not been determined so far. In the present investigation, an intense photograph of the spectrum of a saturated aqueous solution of the substance has been obtained with a spectrograph of high dispersion and high resolving power. Some hitherto unobserved detail has been recorded and the polarisation character of the lines has also been ascertained. The results are discussed in the paper in relation to the structure of the molecule.

2. Experimental Arrangements

The substance used in the present investigation was Kahlbaum's pure chemical and was fairly free from dust. A saturated solution of this substance in double distilled water was rendered dust free by carefully filtering it several times and was finally transferred into a double-walled Wood's tube and sealed off. A few drops of concentrated nitric acid was added to the solution to render it free from fluorescence. The outer jacket of the Wood's tube was filled with a concentrated solution of sodium nitrite solution which reduced the strong continuous background accompanying the Raman spectrum by cutting off all the ultra-violet radiations upto 4046 A.U. Two pyrex mercury arcs placed on either side of the Wood's tube and in close contact with the latter served as intense sources of illumination. A Littrow glass spectrograph having a dispersion of about 10 A° mm. in the 4358 A° region, and a resolving power of about 3 $cm.^{-1}$ in the region between 4046 A° and 4358 A° was employed to obtain the Raman spectrum while the polarisation picture was taken with a Hilger two-prism glass spectrograph of high light-gathering power.

3. *Results*

The Raman frequencies of hexamethylene-tetramine as well as their polarisation characters obtained in the present investigation are listed in Table I along with the results reported by Krishnamurti and Kahovec *et al.*

TABLE I

Raman Frequencies of Hexamethylene-Tetramine

No.	Author	Polarisation	Krishnamurthi	Kahovec *et al.*
1	265 (½) (K.e)	D	..	260 (1) (e)
2	299 (1) ,,	D	..	284 (1) (±e)
3	398 (½) ,,	D	..	..
4	455 (4) ,,	D	457 (m)	454 (4) ±(e, c)
5	514 (2) ,,	D	513 (S)	508 (3) ±(e, c)
6	684 (½) ,,	D	..	682 (½) (e)
7	782 (10) ,,	P	782 (st)	782 (10) (f, e, c)
8	821 (½) ,,	D	820 (S)	818 (0) (e)
9	1009 (3) ,,	D	1008 (m)	1011 (6b) (e)
10	1023 (1) ,,	D	..	..
11	1048 (6) ,,	P	1052 (m)	1046 (6b) (e)
12	1093 (1) ,,	D	..	1090 (2) (e)
13	1240 (2) ,,	D	..	1243 (2) (e)
14	1346 (4) ,,	D	1346 (m)	1345 (5) (e)
15	1384 (2) ,,	D	..	1377 (2) (e)
16	1440 (1) ,,	D	1452 (m)	1451 (5b) (c)
17	1452 (6) ,,	D	..	..
18	2890 (2) ,,	P	..	2873 (3) (e)
19	2965 (2) ,,	P	2948 (st)	2961 (1) (e)
20	2973 (2) ,,	D	..	..
21	2989 (2) ,,	D	2977 (st)	2980 (3) (e)

One new line at $\Delta\nu = 398$ has been obtained in the present investigation in addition to all the frequencies reported by Kahovec *et al.*; while some of the lines reported by these authors as broad have been found to be doublets, *e.g.*, 1011 (6 *b*), 1451 (5 *b*) and 2980 (3). On the other hand the line at 1046, reported as broad by the above authors is found to be quite sharp and intense. These facts can be clearly seen from the spectra reproduced in Plate II.

4. *Discussion*

Gönell and Mark (1923), Dickinson and Raymond (1923), and Wycoff and Corey (1934) have investigated the crystal structure of hexamethylene-tetramine. The unit cell is found to contain two molecules of $C_6H_{12}N_4$. The molecule $C_6H_{12}N_4$ possesses a symmetry Td with atomic distances C–C = 2·58 A° and C–N = 1·48 A°. The carbon atoms thereby occupy the corners of a regular octahedron as seen in Fig. 1. The N atoms which occupy the corners of a tetrahedron lie on the threefold axes of symmetry of the octahedron. The character table, the number of modes of vibration,

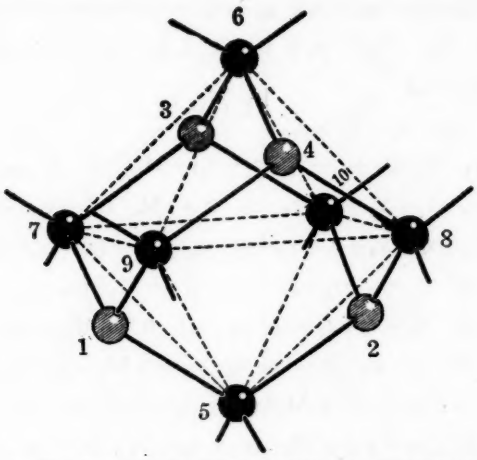

FIG. 1. Structure of Hexamethylene-tetramine molecule $C_6H_{12}N_4$

and the selection rules for the Raman, and Infra-red frequencies are given in Table II.

TABLE II

Character Table for $C_6H_{12}N_4$

Td	E	$8C_3$	$3C_2$	6σ	$6S_4$	Total number of vibrations	Internal vibrations		Translations and Rotations	Selection rule	
							Molecule	Ring		Raman	Infra-Red
A_1 ..	1	1	1	1	1	4	4	2	0	P	f
A_2 ..	1	1	1	−1	−1	1	1	0	0	f	f
E ..	2	−1	2	0	0	5	5	2	0	D	f
F_1 ..	3	0	−1	−1	1	7	6	2	1R	f	f
F_2 ..	3	0	−1	1	−1	10	9	4	1T	D	a
U_R ..	22	1	2	6	0						
$h_j\phi_j$ ..	66	0	−6	36	0						
$h_j\psi_j'$ ..	60	0	0	36	0						

Symmetry Co-ordinates for Ring Frequencies

The principal axes X, Y, Z are obtained by joining the carbon atoms (5, 6), (7, 8) and (9, 10) the positive directions being also the same. The co-ordinates of any mode of oscillation are expressed with respect to a parallel co-ordinate system with its equilibrium position as origin. The following normal co-ordinates are obtained:—

$$\left.\begin{array}{ll} Q_1' & x_1+x_2-x_3-x_4+y_1-y_2+y_3-y_4+z_1-z_2-z_3+z_4 \\ Q_2' & x_5-x_6+y_7-y_8+z_9-z_{10} \end{array}\right] 2A_1$$

$$\left.\begin{array}{ll} Q'_{3a} & y_1-y_2+y_3-y_4-z_1+z_2+z_3-z_4 \\ Q'_{3b} & 2x_1+2x_2-2x_3-2x_4-y_1+y_2-y_3+y_4-z_1+z_2+z_3-z_4 \end{array}\right\} \text{E (1)}$$

$$\left.\begin{array}{ll} Q'_{4a} & y_7-y_8-z_9+z_{10} \\ Q'_{4b} & 2x_5-2x_6-y_7+y_8-z_9+z_{10} \end{array}\right\} \text{E (2)}$$

$$\left.\begin{array}{ll} Q_{wx} & M_N^{\frac{1}{2}}(y_1-y_2-y_3+y_4+z_1-z_2+z_3-z_4)+M_C^{\frac{1}{2}}(z_7-z_8-y_9+y_{10}) \\ Q_{wy} & M_N^{\frac{1}{2}}(x_1-x_2-x_3+x_4+z_1+z_2-z_3-z_4)+M_C^{\frac{1}{2}}(x_9-x_{10}-z_5+z_6) \\ Q_{wz} & M_N^{\frac{1}{2}}(x_1-x_2+x_3-x_4+y_1+y_2-y_3-y_4)+M_C^{\frac{1}{2}}(x_7-x_8+y_6-y_5) \end{array}\right\} \text{F}_1\text{ (1)}$$

$$\left.\begin{array}{ll} Q'_{5a} & 4\,M_C^{\frac{1}{2}}(y_1-y_2-y_3+y_4+z_1-z_2+z_3-z_4)-6\,M_N^{\frac{1}{2}}(z_7-z_8-y_9+y_{10}) \\ Q'_{5b} & 4\,M_C^{\frac{1}{2}}(x_1-x_2-x_3+x_4+z_1+z_2-z_3-z_4)-6\,M_N^{\frac{1}{2}}(x_9-x_{10}-z_5+z_6) \\ Q'_{5c} & 4\,M_C^{\frac{1}{2}}(x_1-x_2+x_3-x_4+y_1+y_2-y_3-y_4)-6\,M_N^{\frac{1}{2}}(x_7-x_8+y_6-y_5) \end{array}\right\} \text{F}_1\text{ (2)}$$

$$\left.\begin{array}{ll} Q_x & M_N^{\frac{1}{2}}(x_1+x_2+x_3+x_4)+M_C^{\frac{1}{2}}(x_5+x_6+x_7+x_8+x_9+x_{10}) \\ Q_y & M_N^{\frac{1}{2}}(y_1+y_2+y_3+y_4)+M_C^{\frac{1}{2}}(y_5+y_6+y_7+y_8+y_9+y_{10}) \\ Q_z & M_N^{\frac{1}{2}}(z_1+z_2+z_3+z_4)+M_C^{\frac{1}{2}}(z_5+z_6+z_7+z_8+z_9+z_{10}) \end{array}\right\} \text{F}_2\text{ (1)}$$

$$\left.\begin{array}{ll} Q'_{6a} & 4\,M_N^{\frac{1}{2}}(x_5+x_6+x_7+x_8+x_9+x_{10})-6\,M_C^{\frac{1}{2}}(x_1+x_2+x_3+x_4) \\ Q'_{6b} & 4\,M_N^{\frac{1}{2}}(y_5+y_6+y_7+y_8+y_9+y_{10})-6\,M_C^{\frac{1}{2}}(y_1+y_2+y_3+y_4) \\ Q'_{6c} & 4\,M_N^{\frac{1}{2}}(z_5+z_6+z_7+z_8+z_9+z_{10})-6\,M_C^{\frac{1}{2}}(z_1+z_2+z_3+z_4) \end{array}\right\} \text{F}_2\text{ (2)}$$

$$\left.\begin{array}{ll} Q'_{7a} & y_1-y_2-y_3+y_4-z_1+z_2-z_3+z_4 \\ Q'_{7b} & x_1-x_2-x_3+x_4-z_1-z_2+z_3+z_4 \\ Q'_{7c} & x_1-x_2+x_3-x_4-y_1-y_2+y_3+y_4 \end{array}\right\} \text{F}_2\text{ (3)}$$

$$\left.\begin{array}{ll} Q'_{8a} & z_7-z_8+y_9-y_{10} \\ Q'_{8b} & x_9-x_{10}+z_5-z_6 \\ Q'_{8c} & x_7-x_8-y_6+y_5 \end{array}\right\} \text{F}_2\text{ (4)}$$

The ten modes of oscillation of the ring are diagrammatically represented in Fig. 2.

Analysis of the Raman Spectrum of Hexamethylene-tetramine

According to group theoretical analysis the sixty vibrational forms of the molecule fall into five classes given in Table II. Most of these vibrations become degenerate due to the high order of symmetry possessed by the molecule. Taking into account the degeneracy as well as the selection rules, 18 frequencies are expected in the Raman Effect and 4 in Infra-red absorption. Out of the 18 frequencies active in the Raman effect 8 are characteristic of the ring and 10 are characteristic of the (C–H) vibrations. All the 8 ring frequencies as well as the 6 deformational (C–H) vibrations ought

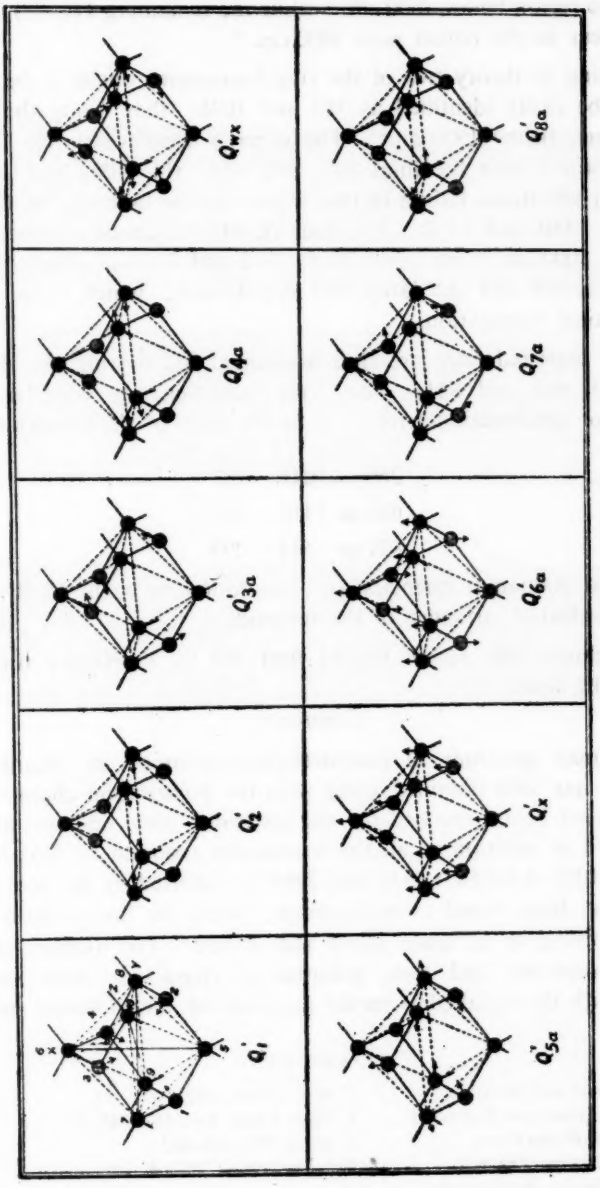

FIG 2

to fall in the region below 1500 cm.$^{-1}$ while the remaining 4 (C–H) frequencies should appear in the region near 3000 cm.$^{-1}$

According to theory two of the ring frequencies ought to be polarised. These can be easily identified as 782 and 1048; they being the only two polarised lines below 1500 cm.$^{-1}$ The other 6 depolarised ring frequencies can be identified with the lines 299, 398, 455, 514, 1009 and 1023 while the 6 (C–H) vibrations falling in this region can be taken to be 1093, 1240 1346, 1384, 1440 and 1452. The four (C–H) frequencies expected in the region near 3000 cm.$^{-1}$ are 2890, 2965, 2973 and 2989 of which the former two are polarised and the latter two depolarised; which is in agreement with theoretical expectation.

All the expected lines are thus accounted for barring the three weak lines at 265, 684 and 821. They may, however, be considered as the differential or combinational tones, as is the case, of the following frequencies:—

$$265 = 1048 - 782$$
$$684 \approx 1452 - 782$$
$$821 \approx 514 + 299.$$

The observed Raman frequencies are thus found to be in good agreement with the tetrahedral structure of the molecule.

In conclusion the author thanks Prof. Sir C. V. Raman for his kind interest in the work.

Summary

The Raman spectrum of hexamethylene-tetramine in saturated aqueous solution has been obtained along with the polarisation character of the lines; the latter being obtained for the first time. One new line at 398 has been observed in addition to all the frequencies reported by Kahovec *et al.* The lines at 1011 (6 *b*), 1451 (5 *b*) and 2980 (3) reported by the above authors as broad have been found to be doublets; while the line at 1046 reported as broad is found to be quite sharp and intense. The number of distinct frequencies recorded and their polarisation characters show satisfactory agreement with the tetrahedral model assigned for the molecule from X-ray studies.

REFERENCES

1. Gönel and Mark .. *Z. Phys. Chem.*, 1923, 107, 181.
2. Dickinson and Raymond .. *J. Amer. Chem. Soc.*, 1923, **45**, 22.
3. Wycoff and Corey .. *Z. Krist*, 1934, **89**, 462.
4. Krishnamurthi, P. .. *Ind. Jour. Phys.*, 1931, **6**, 309.
5. Kahovec, Kohlrausch, Reitz and Wagner .. *Zeit. Phys. Chem.*, 1938, **39 B**, 431.

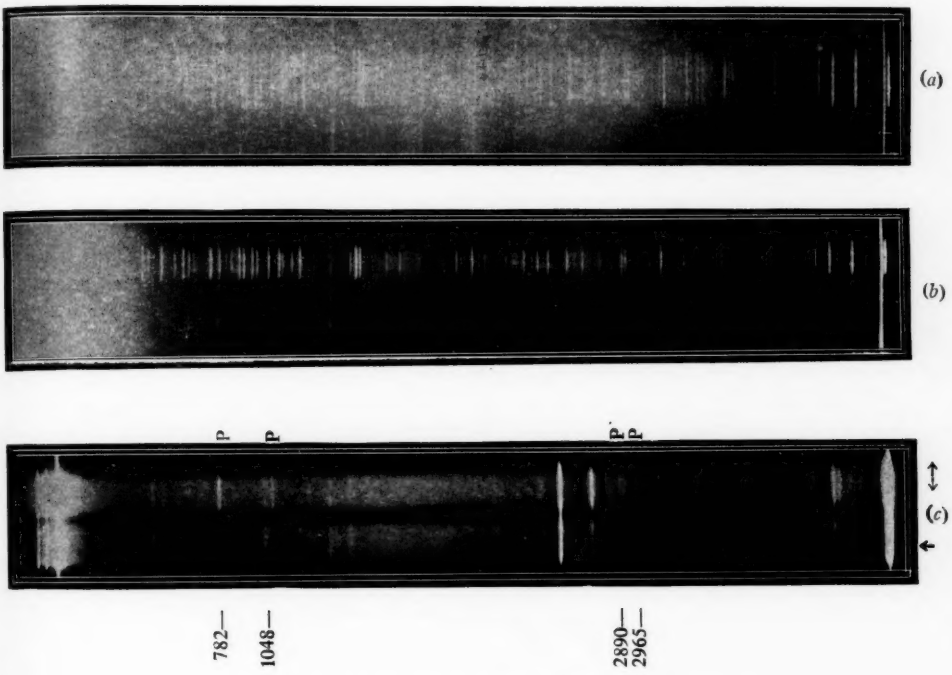

FIG. 3. (*a*) Urotropin without $NaNO_2$ filter
(*b*) Urotropin with $NaNO_2$ filter
(*c*) Polarisation of Urotropin

More recently Sir C. V. Raman (1941, 1943) has reconsidered the problem of the lattice vibrations and has shown that the experimental facts of spectroscopy necessitate a completely new approach to this problem. His theory has been successfully applied by the present author to the evaluation of the specific heats of rocksalt, diamond, and the metals (Dayal, 1944 *a*, *b*, *c*). In the present paper the calculations have been extended to KCl for which an extensive specific heat data is available, and to KBr, the only other crystal of this class which possesses such data.

2. The Frequency Spectrum in the Born and the Raman Theories

Let us for simplicity take the case of a general cubic lattice, the unit cell of which is described by the three equal orthogonal vectors a_1, a_2, a_3. The cells are distinguished by the cell index l where l stands for the three integers l_1, l_2 and l_3. The p different atoms of the cell are indicated by the particle index k. The equilibrium position of the kth atom in the lth cell is given by $r(k, l) = l_1a_1 + l_2a_2 + l_3a_3 + r(k, 0)$ where $r(k, 0)$ is the equilibrium position of the particle in the cell at the origin. According to Born (Born and Goppart Mayer, 1933) the displacement u_k^l of the (l, k)th particle is given by the plane waves of the type

$$u_k^l = \mathbf{U}_k \, e^{i\{-2\pi\nu t + [\mathbf{S}\cdot r(k,l)]\}} \tag{1}$$

The direction of the vector **S** is the direction of propagation of the wave and its magnitude is equal to $\frac{2\pi}{\lambda}$ where λ is the wave-length. The possible values of **S** are determined by the cyclic postulate, according to which the infinite lattice is subdivided into cubic blocks of N^3 cells, N being supposed to be a very large number. It is assumed that the vibration pattern repeats itself exactly in each of these blocks so that the vector **S** is given by

$$\mathbf{S} = 2\pi \left\{ \left(\frac{n_1}{N}\right) b_1 + \left(\frac{n_2}{N}\right) b_2 + \left(\frac{n_3}{N}\right) b_3 \right\} \tag{2}$$

where the b's are the lattice vectors inverse to the a's and n_1, n_2, n_3 are integers given by the condition $-\frac{N}{2} \leqslant n \leqslant \frac{N}{2}$. If the scalar components of the wave-number vector $\frac{1}{\lambda}$ have the values $\frac{1}{\lambda_1}$, $\frac{1}{\lambda_2}$, $\frac{1}{\lambda_3}$, it follows that $\lambda_i = \frac{Na}{n_i}$ where a is the lattice spacing. For the waves travelling along the cube axes λ_i are directly equal to the phase wave-lengths and are the sub-multiples of the length of a side of the large cube of N^3 cells. Because of this assumption, they bear no relation to the crystal spacing and crowd themselves increasingly as they became smaller. It can be easily

seen that one half of them ($\frac{1}{4}$th from each branch, optical and acoustic) have values intermediate between $2a$ and $4a$, $\frac{1}{6}$ between $4a$ and $6a$ and so on, the proportion found in any given range of wave-lengths diminishing continuously and vanishing ultimately for great phase wave-lengths.

The nature of the frequency spectrum in the theory of Born is essentially determined by the cyclic postulate. There are two sections of it namely, the acoustic and the optical branches. The frequencies in the acoustic branch increase continuously from zero which is the value for infinite phase wave-length, to a limiting value in the short wave-region. In the optical branch, the frequency for great phase wave-lengths has a value approximately independent of such wave-length but generally falls off more and more rapidly with the diminishing wave-length, till it reaches its minimum value at the short wave limit. The optical frequencies thus form a continuous spectrum extending between the limiting values of the frequencies corresponding respectively to the infinite and the smallest permissible wave-lengths. Illustrations of its nature will be found in the drawings for the rocksalt crystal given by Kellermann (1940).

On the other hand, the theory of Raman starts from the consideration of the theoretically possible normal modes of vibration of the atoms about their positions of equilibrium in the structure of the crystal. Alike in the case of polyatomic molecules and of continuous systems, the fundamental property of a normal vibration is that all the particles in the system have at any instant the same or the opposite phase of vibration (Rayleigh, 1926). Hence, each of the normal modes with which we are concerned must satisfy this condition and also be consistent with the fundamental property of the crystal, namely, its translational symmetry along each of the three axes of the Bravais lattice. Raman has shown that there are $(24p-3)$ modes of atomic vibration in a crystal which satisfy these requirements. The atomic vibration spectrum thus consists of $(24p-3)$ discrete or monochromatic frequencies, the number, however, being further diminished by degeneracy in the crystals possessing types of symmetry other than that of the translational kind. In these $(24p-3)$ modes, equivalent atoms in the crystal structure possess the same energy of vibration, but the phase of the vibration is either the same for all such atoms along an axis of the Bravais lattice or else is alternately positive or negative. It follows that the $(24p-3)$ modes represent the possible internal vibrations of the atoms contained in a space-unit having 8 times the volume of the lattice cell of the crystal, each of the modes having a degeneracy $^1/_8$th as large as the total number of lattice cells in the crystal. This degeneracy may be regarded as a consequence of the transaltional symmetry of the crystal structure.

Chelam (1943) has discussed the modes of vibration of the NaCl type of lattice on the basis of the Raman dynamics. His results are shown in Table I. It will appear from this that the possible different modes are just those which in Born's theory appear as the limiting vibrations with the greatest and the least possible phase wave-lengths normal to the faces of the cube and the octahedron. Lyddane and Herzfeld (1938) have described the various frequencies of the Born theory by a vector τ the scalar components of which parallel to the cube axes are given by $\tau_i = \frac{2a}{\lambda_i}$. For convenience of reference we have given the values of τ_i corresponding to the Raman frequencies below. Kellermann has used the quantities p_x, p_y, p_z in this connection which can be obtained from the τ_i on multiplication by twenty.

TABLE I. *Modes of Vibration of the Lattice Structure*

Designation and Description of the Mode	Degeneracy	τ_x, τ_y, τ_z
ν_1 Oscillation of the alkali and the halogen lattices against each other	3	0, 0, 0
ν_2 Oscillation of the alkali layers against each other normal to the octahedral planes with the halogen layers at rest	4	¼, ¼, ¼
ν_3 Oscillation of the halogen layers against each other normally to the octahedral planes with the alkali atoms at rest	4	¼, ¼, ¼
ν_4 Same as ν_2 but transversely	8	¼, ¼, ¼
ν_5 Same as ν_3 but transversely	8	¼, ¼, ¼
ν_6 and ν_7 Coupled oscillation of the alkali and halogen ions normal to the cube planes	3, 3	½, 0, 0
ν_8 and ν_9 Coupled oscillation of the alkali and the halogen ions transverse to the cube planes	6, 6	½, 0, 0
Translations	3	0 0 0
Total ..	48	..

3. *The Evaluation of the Frequencies*

Since the discrete frequencies given by the Raman dynamics are included also in the continuous spectrum of the Born theory, it is possible to use the general methods devised by Kellermann (*l.c.*) and others for their evaluation. The displacement of an atom is again given by the equations (1) and (2) but τ is restricted to the values shown in Table I against the Raman frequencies. We have generally followed Kellermann's treatment in the present paper. It is supposed that the potential energy ϕ between any two atoms depends only on the nature of the atoms and their distance of

separation. For the atoms (l, k) and (l', k') it may be written as $\phi_{k\,k'}^{l\,-\,l'}$. The displacement components of the atom (l, k) parallel to the axes are denoted by u_{kx}^{l}, u_{ky}^{l} and u_{kz}^{l} respectively. If the oscillations are harmonic, the force due to the mutual displacement of any two atoms is given by the product of the appropriate force constant and the relative displacement. The force constant being a second differential coefficient of the potential energy, the X component of the force on the atom (l, k) due to the displacement of the atom (l', k') is given by

$$\sum_{y} \frac{\partial^2 \phi_{k\,k'}^{l\,-\,l'}}{\partial x\, \partial y} \; [u_{k'y}^{l'} - u_{ky}^{l}] \tag{3}$$

where the summation is to be carried out for all the three co-ordinate axes. The total force on the atom (l, k) due to the displacements of all the atoms is written as

$$m_k \ddot{u}_{kx}^{l} = \sum_{k'} \sum_{l'} \sum_{y} (\phi_{kk'}^{l\,-\,l'})_{xy} \; u_{k'y}^{l'} \tag{4}$$

with the abbreviations

$$(\phi_{kk'}^{l\,-\,l'})_{xy} = \frac{\partial^2 \phi_{kk'}^{l\,-\,l'}}{\partial x \partial y}$$

and

$$(\phi_{kk'}^{0})_{xy} = - \sum_{k'} \sum_{l}{}' \; (\phi_{kk'}^{l})_{xy}$$

when the dash over the summation sign indicates that the term $l = 0$ and $k = k'$ (the action of the point on itself) is to be excluded. The derivatives are all to be evaluated for the equilibrium positions of the atoms. The displacement of each kind of particle is given by the equation (1) in which $\mathbf{S}_i$ is to be obtained from the τ_i appropriate to the different frequencies. On substitution of (1) in (4) we get

$$4\pi^2 \nu^2 m_k \; U_{kx} + \sum_{k'} \sum_{y} [kk' : xy] \; U_{k'y} = 0 \tag{5}$$

where

$$[kk' : xy] = \Sigma_l \, (\phi_{k'k}^{l})_{xy} \, e^{i\{\mathbf{S} \cdot \mathbf{r}_{k'k}^{l}\}} \tag{6}$$

$\mathbf{r}_{k'k}^{l}$ being the vector joining the equilibrium positions of the $(0, k)$ and the (l, k') atoms. The coupling coefficients (6) occur as the coefficient of the amplitudes U_{ky} in the equation (5). There are six such equations, and on eliminating the amplitudes from them we get a sixth order determinant for the frequencies. For all the modes of vibrations occurring in the Raman dynamics, the determinant splits up into factors so that the solution of the equation is very much simplified. There are mainly two kinds of forces acting between the atoms of the lattice. The first is the electrostatic force between the ions which, because of Coulomb's law, decreases very slowly with the distance. The other is the short range repulsive force which keeps the lattice from collapsing, and is practically confined to the neighbouring

atoms. The summation in the definition of the coupling coefficients is carried out separately for each kind of force. That due to the electrostatic forces alone involves some difficulty and has been carried out for a number of frequencies both by Lyddane and Herzfeld (*l.c.*) and by Kellermann (*l.c.*). The numerical values have been given by them in the units of $\frac{e^2}{a^3}$, where e is the charge on the ion, so that on substitution of the values of these constants the results can be applied to all the NaCl type of lattices. Except for the case $\tau = 0$ the results of both the calculations are the same. For this vibration, Lyddane and Herzfeld have obtained different coefficients for the transverse and the longitudinal waves. Kellermann has questioned the validity of this result and has obtained only one value of the coefficients for all the three modes belonging to this case, the values coinciding with those given by Lyddane and Herzfeld for the transverse vibrations. We will follow Kellermann and use only one set of coefficients for $\tau = 0$.

The evaluation of the coupling coefficients due to the repulsive forces is not very difficult. Lyddane and Herzfeld have used the Born and J. Mayer (1932) expression for the repulsive potential and have thus omitted the small contribution of the Van-der-Waals forces towards the coefficients. Kellermann has, however, taken this into account in a rough way by using the observed value of the compressibility and the equilibrium condition of the lattice. For the actual evaluation of the coefficients, Lyddane and Herzfeld have introduced two constants c_1 and c_2 given by

$$\left.\begin{aligned} \frac{4\pi e^2}{a^3}\, c_1 &= 2\left(\frac{\partial^2 v(r)}{dr^2}\right) r = a \\ \frac{4\pi e^2}{a^2}\, c_2 &= 2\left[\frac{\partial v\,(r)}{\partial r}\right] r = a \end{aligned}\right\} \tag{7}$$

where $v\,(r)$ is the repulsive potential of the ions. Kellermann's constants A and B are 8π times c_1 and c_2 respectively. If we use Kellermann's method, c_2 is the same for all the NaCl type of lattices and is equal to $-\cdot 0466$. c_1 has a different value for each salt and is given by

$$c_1 = \frac{1}{8\pi}\left\{\frac{12a^4}{\kappa e^2} + \frac{4}{3}\,a\right\}, \tag{8}$$

where κ is the compressibility at the absolute zero of the temperature, a the Madelung constant and e the ionic charge. From their calculations for the coupling coefficients, both the authors have obtained the following formulæ for the frequencies. For $\nu_1\,(\tau = 0)$, only Kellermann's expression is given. ω stands for $4\pi\nu$ and μ is the reduced mass.

$$\left.\begin{aligned}
\omega_1^2 &= \frac{4\pi e^2}{\mu a^3}\left[c_1 + 2c_2 - \tfrac{1}{6}\right] \\
\omega_2^2 \text{ and } \omega_3^2 &= \frac{4\pi e^2}{m_k a^3}\left[c_1 + 2c_2 + \cdot 2876\right] \quad (k = 1, \text{ or } 2) \\
\omega_4^2 \text{ and } \omega_5^2 &= \frac{4\pi e^2}{m_k a^3}\left[c_1 + 2c_2 - \cdot 1438\right] \quad (k = 1, \text{ or } 2) \\
\omega_6^2 \text{ to } \omega_9^2 &= \frac{4\pi e^2}{a^3}\left\{\frac{A}{2\mu} \pm \left[\left(\frac{A}{2\mu}\right)^2 - \frac{A^2 - B^2}{m_1 m_2}\right]^{\frac{1}{2}}\right\}
\end{aligned}\right\} \quad (9)$$

where for ω_6 and ω_7 $A = \cdot 1724 + c_1 + 2c_2$

$B = \cdot 5984 - c_1 + 2c_2$

and for ω_8 and ω_9 $A = -\cdot 0862 + c_1 + 2c_2$

$B = -\cdot 2992 + c_1$

In the paper on the specific heats of rocksalt (*l.c.*), we pointed out that the frequencies obtained by Kellermann were slightly lower than those observed in the Raman effect. This is evidently due to the use of the room temperature compressibility in obtaining the constant c_1. In the calculations on KCl we have used the value of the compressibility at 80° K obtained from the measurements of Durand (*l.c.*). For KBr where the low temperature measurements are not available. c_1 has been calculated directly from the experimental value of the infra-red frequency by the use of the formula for ω_1^2 in the equations (9). For KCl we have used $\kappa = 5 \cdot 03 \times 10^{-12}$, $c_1 = \cdot 491$ and $\frac{e^2}{a^3} = 7 \cdot 48 \times 10^3$. In the case of KBr $c_1 = \cdot 506$ and $\frac{e^2}{a^3} = 6 \cdot 4 \times 10^3$. The numerical values of the frequencies are given in Table II below.

TABLE II. *Vibration Frequencies of KCl and KBr*

Frequency Designation	KCl		KBr		Degeneracy
	Cm.$^{-1}$	$\frac{h\nu}{k}$	Cm.$^{-1}$	$\frac{h\nu}{k}$	
ν_1	141	201	113	163	3
ν_2	167	240	156	225	4
ν_3	176	252	109	157	4
ν_4	102	146	97	139	8
ν_5	107	153	68	97	8
ν_6	151	216	100	144	3
ν_7	161	231	143	205	3
ν_8	71·5	102	51·6	74	6
ν_9	147	211	120	172	6

It will be seen that the infra-red proper frequency ν_1 for KCl is exactly the same as the one observed by Barnes (*l.c.*). The use of the infra-red frequency for evaluating c_1 in the case of KBr seems, therefore, to be perfectly justified.

4. Evaluation of the Specific Heats

We have so far considered the nine optical frequencies which comprise 15/16 of the total degrees of freedom of the lattice. In the earlier papers on rocksalt and diamond, we had assigned the 1/16 residual degrees of freedom of translation to the elastic spectrum and had evaluated their contribution to the thermal energy by means of a Debye function. The usual Debye characteristic temperature was, however, divided by $\sqrt[3]{16}$ to allow for the reduced degrees of freedom. We will follow the same method here. The Debye characteristic temperature for KCl as evaluated by Durand from the elastic constants at 80° K. is 246, but the value which best explains the experimental data near 3° K. is 228. According to Blackman (1935), the two values should be the same. In view of the large uncertainty which is usual in the determination of the elastic data, we have used 228 as the correct Debye characteristic temperature. The reduced value is accordingly 90. Blackman (1938) has given 179 as the value of the characteristic temperature for KBr, from which we have obtained the reduced value as 71 for the purpose of these calculations. c_v are given by the formula

$$C_v \text{ (molar)} = \frac{3R}{24}\left[\sum_1^9 n_s \, E\left(\frac{h\nu_s}{kT}\right) + 3D\left(\frac{\theta_D}{T}\right)\right] \qquad (10)$$

n_s stands for the number of degrees of freedom pertaining to the frequency ν_s, while E and D stand for the Einstein and the Debye functions respectively. The experimental data for KCl have been taken from Keesom and Clark for (3–17)° K. and from Southard and Nelson above that temperature. The former experimenters have pointed out that on account of the small quantity of KCl used for the specific heat determinations, the accuracy of their results is not very high, while the latter have claimed an accuracy of less than one per cent. C_v have been taken from Venkateswaran's paper (1941) who has given the expression $2c_p^2T$ for $(c_p - c_v)$. For KBr, c_v is taken from Nernst and Lindemann (1911 *l.c.*). The last two readings are mean values over an extended range of temperature. The calculated values of c_v for KCl and KBr are given in Tables III and IV respectively.

TABLE III. *Specific Heats of KCl in Cals. gm. mol. deg.*

Temperature °K	Optical frequencies	Elastic spectrum	Total C_v	Experimental C_v
2·99	..	·00215	·00215	·00206
3·52	..	·00348	·00348	·00338
4·01	..	·0052	·0052	·0042
4·6	..	·0077	·0077	·0072
5·72	..	·0149	·0149	·0145
6·52	..	·022	·022	·019
7·65	..	·0353	·0353	·0368
9·2	·0028	·0601	·0629	·0620
10·06	·0062	·0767	·0829	·0840
14·73	·087	·190	·277	·310
17·09	·186	·253	·439	·458
21·21	·475	·349	·824	·842
32·41	1·830	·521	2·351	2·358
39·86	2·935	·585	3·520	3·520
49·27	4·278	·633	4·91	4·91
59·61	5·548	·667	6·22	6·30
69·92	6·555	.686	7·24	7·33
79·11	7·287	·698	7·99	8·12
89·28	7·927	·708	8·64	8·77
101·31	8·537	·716	9·25	9·35
121·41	9·205	·724	9·93	10·04
141·17	9·670	·729	10·40	10·60
163·45	10·006	·733	10·74	10·96
179·76	10·201	·735	10·94	11·13
201·32	10·395	·737	11·13	11·32
240·7	10·63	·74	11·37	11·58

TABLE IV. *Specific Heats of KBr in Cals. deg. gm. mol.*

Temperature °K	Optical frequencies	Elastic spectrum	Total C_v	Experimental C_v
78·7	8·452	·715	9·17	9·42
82·5	8·659	·718	9.38	9.46
85·4	8·802	·719	9·52	9·58
89·2	8·968	·721	9·69	10·00
137	10·133	·734	10·87	10·66
234	10·795	·741	11·54	11·74

In conclusion, the author expresses his grateful thanks to Professor Sir C. V. Raman, KT., F.R.S., N.L., for his guidance in the course of this work.

Summary

The specific heats of KCl and KBr have been evaluated on the basis of the Raman theory of lattice vibrations. The nine discrete frequencies required by the theory and comprising 15/16th of the total degrees of freedom of the crystal have been calculated on the lines followed by Kellermann and by Lyddane and Herzfeld. The electrostatic coupling coefficients

have been taken from the work of the above authors, while the repulsive coefficients have been calculated from the low-temperature value of the compressibility and the equilibrium condition of the lattice. In the case of KBr where the low temperature value of the compressibility is not available, one of the repulsive coefficients has been calculated from the known value of the infra-red frequency. The residual 1/16 of the degrees of freedom not covered by the optical frequencies has been allotted to the elastic spectrum whose contribution to the thermal energy has been evaluated by using a Debye function with a greatly reduced characteristic temperature. An excellent agreement between the theoretical and the experimental values of c_v has been obtained throughout the entire range of temperature.

REFERENCES

Barnes	..	*Zeits f. Physik*, 1932, **75**, 723.
Blackman	..	*Proc. Roy. Soc.*, 1935 (A), **149**, 117; **164**, 62.
———	..	*Proc. Phys. Soc.*, 1942, **54**, 377.
Born and Goppart Mayer	..	*Handbuch der Physik, Berlin*, 1933.
Born and J. Mayer	..	*Zs. f. Physik*, 1932, **75**, 1.
Chelam	..	*Proc. Ind. Acad. Sc.*, A 1943, **18**, 261.
Dayal	..	*Ibid.*, 1944, **19**, 182, 224; **20**, 24.
Durand	..	*Phys. Rev.*, 1936, **50**, 449.
Försterling	..	*Ann. der Physik*, 1920, **61**, 549.
———	..	*Zeits. f. Physik*, 1920, III, 12 ; **8**, 251.
Honnefelder	..	*Zeits. f. Phys., Chem.*, 1933, **21 B**, 53.
Keesom and Clark	..	*Physica*, 1935, **2**, 698.
Kellermann	..	*Phil. Trans. Roy. Soc.*, (A) 1940, **238**, 513.
———	..	*Proc. Roy. Soc.*, (A) 1941, **178**, 17.
Lyddane and Herzfeld	..	*Phys. Rev.*, 1938, **54**, 846.
Nernst and Lindemann	..	*Zeits. f. electrochm.*, 1911, **17**, 817.
———	..	*Sit. Per. Akad.*, 1912, 1160.
Raman	..	*Proc. Ind. Acad. Sc.*, (A) 1941, **14**, 459 ; 1943, **18**, 237.
Rayleigh (Lord)	..	*Theory of Sound*, Vol. I, Macmillan, London, 1926, p. 107.
Rose	..	*Phys. Rev.*, 1936, **49**, 50.
Thirring	..	*Phys. Zeits.*, 1914, **15**, 127, 180.
Venkateswaran	..	*Proc. Ind. Acad. Sc.*, (A) 1941, **14**, 506.

THE SPECIFIC HEAT OF METALLIC SILICON

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1. Introduction

Silicon crystallises in the cubic system with a diamond-like structure but, contrary to the general belief about the applicability of the Debye function to the cubic crystals, its thermal energy is not capable of being explained on the Debye theory. Its specific heats have been measured over an extensive range of temperature between 20 and 1000 degrees absolute. The characteristic temperature which best explains the experimental data at high temperatures has been given by Magnus (1923) as 712, but as the temperature is lowered, the experimentally observed specific heat gradually becomes greater than the value calculated from the Debye function, and at 40° K., the former becomes four times as large as the latter. So far, the only attempt to explain this so-called anomaly has been made by Simon (1926) on the basis of Schottky's quantum jump theory. He considers the specific heat as made up of two parts. The first is the normal part of the specific heat which is given by a Debye function ($\theta = 790$), while the second is attributed to the presence of the two distinct atomic states in the lattice which are independent of the normal modes. The contribution of the latter to the atomic heat is assumed to be given by a Schottky function ($U = 246$). This theory has been criticised by Fowler (1935, 1936) who finds no *a priori* justification for assuming the existence of two distinct atomic states in such cases. According to him, these specific heat anomalies arise from the fact that the Debye theory does not give the correct vibration spectrum of the solid.

More recently Sir C. V. Raman (1941, 1943) has reconsidered the nature of the vibration spectrum of solids and has shown that it is completely different from the continuous spectrum given by the Debye theory. The present author has found (Dayal, 1944 *a-d*) that the specific heats of the alkali halides, diamond and the metals can be completely accounted for on the basis of the new theory. In the present paper it is proposed to extend the investigation to the case of silicon.

2. Evaluation of the Frequencies

In the analogous case of diamond, the vibration spectrum is completely known as a result of the spectroscopic investigations. All that is

necessary is to assign the frequencies to their respective modes of vibration and thus to determine their degeneracies. This has been done (Dayal, 1944 *b*) on the basis of the theoretical formulæ of Bhagavantam (1943) and of Chelam (1943) with the help of three force-constants, two of which, namely (K and K″), arise from the mutual displacements of the neighbours and next nearest neighbours respectively, while the third Kα is involved in the changes of the various valence angles. In the absence of any experimental knowledge of the frequencies in the case of silicon, they have been directly calculated from a set of three force-constants appropriately assumed. The force constants chosen are

$$K = 1{\cdot}2 \times 10^5 \text{ dynes/cm.}$$
$$K'' = 0{\cdot}36 \times 10^5 \text{ dynes/cm.}$$
$$K_\alpha = -0{\cdot}07 \times 10^5 \text{ dynes/cm.}$$

The calculated values of the frequencies with their respective degeneracies are given in Table I. These degeneracies refer to the vibrations in a supercell which is the unit of the vibration pattern and has twice the linear dimensions and eight times the volume of the unit cell of the crystal lattice. Each degree of freedom of this supercell has a degeneracy of N/16 in the whole lattice arising out of the translational symmetry.

The choice of the three force-constants, it should be remarked, has not been made in an arbitrary fashion, but is based on the experimental data. Stitt and Yost (1937) have found that the frequency of vibration of the two SiH_3 groups against each other in disilane (Si_2H_6) has the value 434·5 cm.$^{-1}$, from which they deduced $1{\cdot}7 \times 10^5$ dynes/cm. as the force-constant for the Si—Si bond. The force-constant for the C—C bond in the analogous carbon compound, namely ethane, has been found by Bonner (1937) as $4{\cdot}3 \times 10^5$ dynes/cm. The force constant K in diamond was found by us (l.c.) to be smaller than that in ethane and could be obtained from it on division by 1·4. We have, therefore, obtained K in the case of silicon by reducing the Si—Si force constant for disilane in the same ratio. The force constant K″ has been approximately obtained from the observed compressibility. Nagendra Nath (1935) has shown that the compressibility β of diamond is given by the formula

$$\beta = \frac{3d}{(K + 8K'')}$$

where d is the lattice constant. The compressibility of silicon calculated from this formula and the assumed force constants is $0{\cdot}39 \times 10^{-12}$ cm.^{2}dyne, which compares well with the observed value $0{\cdot}32 \times 10^{-12}$ (Richards, 1915). The third force constant Kα was found to be 1/16th of the force-constant K

in the case of diamond. The ratio of K to Kα is the same in the present case also, but whereas Kα was positive in diamond, it has a negative sign here. We have found (Dayal, 1944 *c*) that the deformation force-constant δ is always negative in the case of metals. A negative sign for Kα is thus in keeping with the metallic character of silicon.

TABLE I

Vibration Frequencies of Silicon

No.	Mode*	Frequency		Degeneracy
		Cm.$^{-1}$	$\frac{h\nu}{k}$	
ν_1	F_2	321	460	3
ν_2	H_1	463	660	6
ν_3	H_2	190	273	6
ν_4	H_4	523	750	6
ν_5	K_3	563	805	4
ν_6	K_1	363	520	4
ν_7	M_1	438	620	8
ν_8	M_2	134	192	8

* The symbols F_2, etc., denote the group theoretical symbols used by Bhagavantam (*l.c.*).

3. *Evaluation of the Specific Heats*

In our work on diamond we had represented the residual 1/16th of the total degrees of freedom, not covered by the eight optical frequencies, by a Debye function. In order to take the smaller number of degrees of freedom into account, the usual characteristic temperatures was however, divided by $\sqrt[3]{16}$. We have used the same method here. The elastic constants being unknown, they were evaluated from the above force constants by the use of Nagendra Nath's formulæ (*l.c.*). The values obtained are:

$$c_{11} = 2{\cdot}89 \times 10^{12} \text{ dyne/cm.}^2 \quad c_{12} = 2{\cdot}34 \times 10^{12} \text{ dyne/cm.}^2$$
$$c_{44} = 5{\cdot}54 \times 10^{11} \text{ dyne/cm.}^2$$

The characteristic temperature was obtained from the average value of $1/v^3$ (v = velocity of elastic waves) along the cube axes and the cube diagonals, the statistical weight in taking the average being 3 and 4 along these directions respectively. The calculated θ is 530 and the reduced value is 210. The formula for C_v then becomes

$$C_v = \frac{3R}{48}\left[\sum_1^8 n_s \, E\left(\frac{h\nu_s}{kT}\right) + 3D\left(\frac{210}{T}\right)\right]$$

where E and D stand for the Einstein and the Debye functions respectively. n_s is the number of degrees of freedom of the supercell corresponding to the

frequency ν_s and is given in the last column of Table I. The calculated atomic heats are given in Table II.

The specific heats C_p of this substance have been measured by Nernst and Schwers (1914) at a few temperatures between (20–90)° K., by Anderson (1930) from (61-296) ° K., and by Magnus (1923) from (138-1,000)° K. Nernst and Schwers' values are considerably (2 to 30%) lower than those extrapolated by Anderson from his own data. We have shown only the latter's extrapolated values in Table II in this region. $(C_p—C_v)$ has been taken from our earlier work (Dayal, 1941) where it was calculated from the approximate formula $(C_p—C_v) = AC^2_p T$. A was obtained from the linear coefficient of expansion $(7{\cdot}15 \times 10^{-6})$, and the compressibility $(\cdot 325 \times 10^{-12})$, the values having been taken from the *International Critical Tables* for 23° C. Since, however, the linear coefficient of expansion as measured by different workers varies between $(2{\cdot}8$ to $7{\cdot}3) \times 10^{-6}$ (*I. C. Tables*, Vol. I, page 104), the correction is extremely uncertain. The uncertainty in the values of C_v due to this cause is only important at very high temperatures and may be as high as 3-4% in the neighbourhood of 700°K.

TABLE II

Atomic Heats of Silicon in Cals./Deg. Gm. atom

Temp. ° K.	Optical frequencies	Elastic spectrum	Total C_v	Experimental C_v	Literature
20·1	·007	·025	·032	·042	Anderson (extrapolated)
28·2	·055	·062	·117	·123	,,
39·7	·224	·125	·349	·336	,,
53·1	·492	·190	·682	·630	,,
61·2	·664	·222	·886	·811	Anderson (experimental)
65·1	·743	·233	·976	·974	,,
75·0	·949	·259	1·208	1·160	,,
98·8	1·435	·301	1·736	1·695	,,
116·7	1·809	·318	2·127	2·152	,,
129·8	2·067	·324	2·391	2·429	,,
145·5	2·384	·345	2·729	2·740	,,
158·8	2·631	·345	2·976	2·993	,,
165·8	2·845	·346	3·191	3·156	,,
186·9	3·102	·349	3·451	3·496	,,
199·2	3·262	·353	3·615	3·684	,,
213·6	3·473	·354	3·827	3·841	,,
237·5	3·753	·358	4·111	4·076	,,
253·3	3·918	·359	4·277	4·335	,,
283·3	4·173	·362	4·535	4·566	,,
350	4·591	·366	4·957	4·972	Magnus
400	4·797	·367	5·164	5·094	,,
500	5·128	·370	5·498	5·298	,,
700	5·301	·371	5·672	5·558	,,
1000	5·427	·372	5·799	5·622	,,

In conclusion, the author wishes to record his grateful thanks to Professor Sir C. V. Raman, KT., F.R.S., N.L., for the interest taken by him in this work.

4. *Summary*

The specific heats of silicon have been evaluated on the basis of the Raman theory of crystal vibrations. The eight discrete frequencies indicated by the theory have been calculated from force constants based on the Raman effect data of disilane and the observed compressibility of silicon. The residual 1/16th of the total degrees of freedom of the crystal, not covered by the eight discrete frequencies, have been assigned to the elastic spectrum and their contribution to the specific heats has been evaluated by a Debye function with a correspondingly reduced parameter. This has been obtained from the elastic data deduced theoretically from the force constants. There is an excellent agreement between the calculated and the observed values of the specific heats throughout the entire range of temperature (20-1,000)° K.

REFERENCES

Anderson .. *J. A. Chem. Soc.*, 1930, **52**, 2301.

Bhagavantam .. *Proc. Ind. Acad. Sci.* (A), 1943, **18**, 251.

Bonner .. *J. Chem. Phys.*, 1937, **5**, 297.

Chelam .. *Proc. Ind. Acad. Sci.* (A), 1943, **18**, 334.

Dayal .. *Ibid.*, 1941, **14**, 473 ; 1944, **19**, 182, 224 ; (*c* and *d*) July issue.

Fowler .. *Proc. Roy. Soc.* (A), 1935, **151**, 1.

——— .. *Statistical Mechanics*, Cambridge, 1936, p. 131–32.

Magnus .. *Ann. der Physik.*, 1923, **70**, 325.

Nagendra Nath .. *Proc. Ind. Acad. Sci.* (A), 1935, **1**, 841.

Nernst and Schwers .. *Per. Akad. Wissen. Berl.*, 1914, 355.

Raman .. *Proc. Ind. Acad. Sci.* (A), 1941, **14**, 459 ; 1943, **18**, 237.

Richards .. *J. A. Chem. Soc.*, 1915, **37**, 1643.

Simon .. *Per. Akad. Wissen. Berl.*, 1926, 477.

Stitt and Yost .. *J. Chem. Phys.*, 1937, **5**, 94.

THE THERMAL EXPANSION OF DIAMOND

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1. Introduction

Diamond has been the subject of numerous studies at this Institute during recent years. Nayar (1942), Miss Mani (1944) and R. S. Krishnan (1944) have investigated the vibration spectrum of its crystal lattice, and the latter has identified 1332, 1284, 1248, 1149, 1088, 1103, 784 and 565 as its characteristic frequencies expressed in wave-numbers. The presence of so large a number of discrete optical frequencies in a crystal with only two non-equivalent atoms in the unit cell has been explained by Sir C. V. Raman (1943) on the basis of a new theory of the vibrations of crystal lattices. Bhagavantam (1943) and Chelam (1943) have obtained expressions for the normal modes of the diamond lattice on the basis of this theory, and Dayal (1944) has correlated these frequencies with the known specific heat data of Pitzer (1938) below 273° A and of Magnus and Hodler (1926) above this temperature. Nayar (1941) has studied the scattering of light in diamond over a wide range of temperatures and finds that the principal Raman line with the frequency shift of 1332·1 cm.$^{-1}$ at 25° C. remains sensibly sharp over the whole range of temperature from 85° A to 1130° A, the frequency shift at first diminishing slowly and then more rapidly with rising temperature, being 1333·8 and 1316·4 respectively at the two extremes of the range. These frequency changes are evidently determined by the thermal expansion of diamond, and although the data regarding the latter are rather scanty, it appears worthwhile to review the existing theories in the light of the observed facts.

2. Theoretical Basis of Grüneisen's Formula

Grüneisen was the first to suggest that the co-efficient of expansion of a crystal is related to its specific heat, and showed this to be the case for several metals. The relation has come to be regarded as a fundamental one in the theory of the solid state, and several proofs of its validity have been suggested. Grüneisen himself (1912, 1926 *a*) assumed a law of force between the atoms

in which the attractive and repulsive forces varied as the mth and nth power of the distance between the atoms and was thus led to his well-known relation

$$\frac{V - V_0}{\chi_0} = \frac{\gamma E}{1 - \frac{m+n+3}{6}\gamma \frac{\chi_0}{V_0} E} \tag{1}$$

or

$$\alpha = \frac{1}{V_0}\frac{dV}{dt} = \frac{\gamma C_v \chi_0}{V_0} \tag{2}$$

(neglecting the expression $\frac{m+n+3}{6}\gamma \frac{\chi_0}{V_0} E$ which is very small).

χ_0 is here the compressibility at zero temperature, E the energy, $\gamma = \frac{-\partial \log \nu}{\partial \log V}$; α is the thermal expansion coefficient, C_v the atomic heat and V_0 the atomic volume. Debye, on the other hand, deduced from thermodynamic considerations the equation of state for monoatomic isotropic bodies in the form $\left(p + \frac{d\phi}{dV}\right) V = -\frac{\partial \log \nu}{\partial \log V} E$, E being the thermal energy. From this equation, Grüneisen's relation follows as a first approximation.

Dynamically, a crystal can be approximated by a set of 3N vibrations with frequencies $\nu_1, \nu_2 \ldots \nu_{3n}$, there being n atoms in the crystal. If the anharmonicity is small, it can be shown (Slater, *a*) that the coefficient of thermal expansion is given by $\alpha = \frac{\chi_0 k}{V_0} \Sigma \gamma_j \frac{x^2 e^x}{(e^x - 1)^2}$ where $x = \frac{h\nu_j}{kT}$ and $\gamma_j = -\frac{\partial \log \nu_j}{\nu \log V}$. Grüneisen assumed that all the ν_js were equal to each other in a regular monoatomic lattice, so that γ may be regarded as an empirical constant. We have then Grüneisen's relation in the form already stated.

The justification for Grüneisen's formula (Slater, *b*) comes from the Debye theory giving $\gamma = -\frac{\partial \log \nu_{max}}{\partial \log V}$, according to which the frequency spectrum is entirely determined by the limiting frequency ν_{max} and if this frequency changes, all other oscillations change their frequences in the same ratios. Grüneisen (1926, *c*) found support for his formula in the case of diamond. Taking the Debye temperature θ to be 1860 as found by Nernst and Lindemann from the specific heat data, he found an agreement between the observed and calculated values of the thermal expansion. We shall, however, now re-examine the situation in the light of Nayar's spectroscopic data.

3. *The Failure of Grüneisen's Formula*

We have $\gamma = -\frac{\partial \log \nu}{\partial \log V} = -\frac{1}{\nu}\cdot\frac{\Delta\nu}{T_2 - T_1}\cdot\frac{1}{\bar{\alpha}}$ where $\bar{\alpha}$ is the mean coefficient of thermal expansion and $\Delta\nu$ the diminution in frequency ν in the termperature range T_1 to T_2.

$$\therefore \quad \Delta\nu = \gamma\bar{\alpha}(T_2 - T_1)\nu \qquad (3)$$

We use equation (2) to find $\bar{\alpha}$ the mean coefficients of thermal expansion and equation (3) to find the diminution in frequency of the line 1332·1 (25°) in diamond with the rise of temperature. We need the mean values of the specific heats at constant volume. The latest specific heat data (C_v) are by Pitzer below 273° A and by Magnus and Hodler above this temperature. These have been plotted on a curve and from it $\bar{C}_v$ was obtained by finding the area $\int_{T_1}^{T_2} C_v\,dT$ and dividing it by $(T_2 - T_1)$. The bulk modulus of diamond at 20° C. has been determined by Adams (1921) and Williamson (1922). Their values are respectively $6{\cdot}25 \times 10^{12}$ and $5{\cdot}56 \times 10^{12}$. Grüneisen found a value of $\gamma = 1{\cdot}1$ by using the first value. We shall also use this value of γ in the present calculation. The observed values of the mean coefficient of thermal expansion are those of A. Dembowska (quoted by Grüneisen, *c*). The results of the calculation are shown in Table I. We

TABLE I

Temp. Range Å	$\bar{C}_v$ or Mean value of C_v	Mean value of thermal expansion $\bar{\alpha}$		$\Delta\nu$	
		Calculated $\times 10_6$	Observed $\times 10_6$	Calculated	Observed (Nayar)
84·8– 194·1	·2333	·502	·54	..	..
194·1– 273·2	·866	1·860	1·74	..	..
273·2– 296·2	1·351	2·907	2·91	..	..
296·2– 328	1·605	3·452	3·51	..	..
328 – 351·1	1·870	4·02	4·35	..	..
300 – 400	1·963	4·224	..	·62	1·2
400 – 500	2·921	6·284	..	·92	1·4
500 – 600	3·691	7·939	..	1·16	1·6
600 – 700	4·166	8·962	..	1·31	1·9
700 – 800	4·466	9·607	..	1·41	2·0
800 – 900	4·710	10·14	..	1·48	2·2
900 –1000	4·913	10·57	..	1·55	2·4
1000 –1100	5·041	10·84	..	1·59	2·55

use χ_{293} instead of χ_0 as the difference would be very small for a crystal of extremely low compressibility like diamond. For higher temperatures Grüneisen includes in equation (1) the correction term $\frac{m+n+3}{6}\gamma\frac{\chi_0}{E_0}E_v$

although he neglects it for the region in which the thermal expansion data are available for diamond.

According to Grüneisen, $\frac{m+n+3}{6}$ should lie between 2 and 3. $\frac{V_0}{\gamma\chi_0} = 457$ K. calories for diamond and $E_{1100} = 3{\cdot}3$ K. cal. Using the maximum value 3 for $\frac{m+n+3}{6}$ we get a maximum increase of 2% in the calculated value of α in the highest temperature region. Further, the mean values of c_p should have been used in the above calculation. These however differ from the C_v values by only 1% at the highest temperatures. The calculated value at high temperatures of $\Delta\nu$ is thus only very slightly (to the extent of 3%) affected by using C_v and neglecting the correction term. We find from Table I that though the Grüneisen constant 1·1 gives a fairly satisfactory agreement between the observed and calculated values of α, it completely fails to fit Nayar's spectroscopic observations.

4. *Thermal Expansion on the New Lattice Theory*

The lattice spectrum of a crystal according to Sir C. V. Raman exhibits, in general, $(24p - 3)$ monochromatic modes of vibration, p being the number of non-equivalent atoms in the basis cell. These are the modes of vibration of the atoms in a super-cell having the twice dimensions and eight times the volume of the unit cell. The three missing degrees of freedom represent the elastic spectrum of the solid. Accordingly, the mean coefficient of thermal expansion may be written as

$$\alpha = \frac{\chi_0}{V_0}\frac{3RJ}{24p}\left\{\sum_1^{24p-3}\sigma_i C_{v_i}\frac{\partial \log \nu_i}{\partial \log V} + 3\,D(\nu_m)\frac{\partial \log \nu_m}{\partial \log V}\right\}$$

In this equation C_{v_i} represents the contributions of the monochromatic frequencies ν_i to the specific heat C_v and σ_i is the statistical weight of frequency ν_i and $\frac{\partial \log \nu_i}{\partial \log V} = \gamma_i$ is its volume dependence. It has been shown thermodynamically that if we assume γ to be the same for all frequencies, γ is independent of temperature even at low temperatures (Mott and Jones). We take therefore γ_i to be independent of temperature. For obtaining the mean values of ermal expansion, we have to form energy differences so that

$$\bar{\alpha} = \frac{P_2(U) - P_1(U)}{T_2 - T_1}$$

where $$P(U) = \frac{\chi_0}{V_0}\frac{3RJ}{24p}\left[\sum_1^{24p-3}\gamma_i\sigma_i E(U) + 3\,\gamma_m D(U)\right]$$

E (U) and D (U) being the Einstein and Debye energy functions.

The frequencies of the diamond lattice are: $\underset{3}{\overset{\nu_1}{1331}}$ $\underset{8}{\overset{\nu_2}{1284}}$ $\underset{6}{\overset{\nu_3}{1248}}$ $\underset{6}{\overset{\nu_4}{1149}}$ $\underset{4}{\overset{\nu_5}{1088}}$ $\underset{4}{\overset{\nu_6}{1013}}$ $\underset{6}{\overset{\nu_7}{784}}$ $\underset{8}{\overset{\nu_8}{565}}$, the number below each frequency indicating its statistical weight according to Dayal. The Debye limiting frequency has been calculated as $\nu_D = 573$ and has weight 3. We have no knowledge of the volume dependence of these frequencies, and we have therefore to make some reasonable assumptions regarding their γ values which will fit Nayar's data as also the observed values of expansion cofficient. The higher frequencies 1332, 1284, 1248, 1149, 1088 and 1013 represent modes of vibration in which the distances between neighbouring carbon atoms alter and are determined by the binding forces between them, while the lowest two frequencies 784 and 565 do not involve any variation of the distance between the carbon atoms linked with each other. We divide the frequencies into these two groups and assume that all the frequencies in each group have the same value of γ. Further, there is no reason to suppose that the transverse modes of vibration in the elastic spectrum would have the same volume dependence as the longitudinal modes, since the nature of the two modes is essentially different. We therefore divide the elastic spectrum into two branches, *viz.*, the longitudinal and transverse branches, the former with statistical weight one and the latter with weight two. We find by calculation $\nu_l = 842{\cdot}5$ and $\nu_t = 514$. These values give good agreement with the observed specific heat data. We include ν_l in the group of higher frequencies and assume the same value of γ for it and ν_t in the group of lower frequencies with a different γ. We thus need only two different γ values for the crystal, γ_c for the group of higher frequencies and γ_t for the group of lower frequencies. We accordingly write P (U) in the form

$$P(U) = \frac{\chi_0}{V_0}\frac{3RJ}{48}[\gamma_2\{3E_1(U) + 8E_2(U) + 6E_3(U) + 6E_4(U) + 4E_5(U) + 4E_6(U) + D_8(U)\} + \gamma_t\{6E_7(U) + 8E_8(U) + 2D_t(U)\}]$$

where $E_1(U)$, etc., are Einstein energy functions for the 8 monochromatic frequencies and $D_c(U)$ and $D_t(U)$ are the Debye energy functions for the longitudinal and transverse Debye frequencies.

We have chosen $\gamma_c = 1{\cdot}402$ and $\gamma_t = 0{\cdot}834$ to fit Nayar's data as also the thermal expansion coefficients. In choosing two constants which fit two separate sets of data, we are not really assuming two arbitrary constants which can be varied at will. Moreover, it is *prima facie* evident that the modes of vibration which involve change in the C – C bond length would contribute to the thermal expansion in a larger measure than those which do not.

As diamond is a homopolar crystal, we may use the method given by Slater (*c*) for finding γ.

$$\gamma = \frac{ar_0}{2} + \frac{1}{3} \text{ and } (ar_0)^2 = \frac{9\,Ncr_0^3}{2L\,\chi_0}$$

where L is the heat of dissociation, $c = 8/3^{3/2}$, r_0 the C—C distance, χ_0 the compressibility, and N the Avagadro number. For diamond; $L = 72{\cdot}6$ K. cal. per gram atom (Fajans, 1920, 1922) and $r_0 = 1{\cdot}54 \times 10^{-8}$ which gives $\gamma = 1{\cdot}17$ if $\chi_0 = 0{\cdot}180 \times 10^{-12}$. It will be noticed that this is about the same as the value of γ assumed by Grüneisen and lies midway between the values of γ_e and γ_t found above.

5. *Calculation of Thermal Expansion Co-efficients*

We use $\chi_0 = 0{\cdot}18 \times 10^{-12}$ which is the value obtained from the latest work of Williamson. The results of the calculation are shown in Table II.

TABLE II

Temp. Region	$\bar{a} \times 10^6$		$\Delta\nu$	
	Calc.	Obs.	Calc.	Obs.
84·8– 194·1	·49	·54	..	..
194·1– 273·2	1·85	1·74	..	..
273·2– 296·2	3·15	2·91	..	..
196·2– 328	3·64	3·51	..	..
328 – 351·1	4·31	4·35	..	..
194·1– 296·2	2·19	..	·41	·8
296·2– 400	4·52	..	·88	1·2
400 – 500	6·82	..	1·28	1·35
500 – 600	8·72	..	1·63	1·60
600 – 700	10·16	..	1·90	1·85
700 – 800	11·25	..	2·08	2·0
800 – 900	12·13	..	2·24	2·2
900 –1000	12·77	..	2·36	2·4
1000 –1100	13·23	..	3·20	3·3

We find from Table II that the thermal expansion data and the spectroscopic data of Nayar are both reasonably well fitted. There is some divergence between the observed and calculated values of $\Delta\nu$ in the low temperature region, but this is most likely due to the difficulty of measuring the very small frequency changes in this region. In the high temperature region the agreement is remarkably good.

Using the same values of γ_e and r_t, we have also calculated the co-efficients of thermal expansion at 20° C., 40° C., 50° C. for which the data are available from the *I. C. Tables* and *Physico-Chemical Tables*, Vol. I, p. 17.

Temp. ° C.	$a \times 10^6$(Calc.)	$a \times 10^6$ (Obs.)	Observer
20	3·02	2·7	I.C.T.
		2·91	H.B.P.
40	3·64	3·54	Fizeau P.C.T.
50	3·88	3·96	Fizeau P.C.T.

(Grüneisen gives the values of α at 20° C. as $2{\cdot}91 \times 10^{-6}$). The calculated values show good agreement with the observed values of Fizeau.

It is to be noted that the values of the co-efficient of thermal expansion calculated by us for the region of higher temperatures (*vide* Table II) are greater than those calculated on the basis of Grüneisen's formula (Table I). This is a point which can be tested out experimentally.

In conclusion the author thanks Professor Sir C. V. Raman, for his kind suggestions and keen interest in the work.

6. *Summary*

It is shown that the well-known Grüneisen's law of thermal expansion does not fit in with Nayar's observations of the change of the Raman frequency shift in diamond with temperature, although it gives a fairly good agreement between the observed and calculated values of thermal expansion in the lower ranges of temperature for which alone data are at present available. The assumption of a single Grüneisen constant for diamond is not in agreement with the facts and does not appear to be justified. The expression for thermal expansion on the basis of the new lattice theory of Raman has been written down. The frequencies have been divided into two groups, one of higher and the other of lower frequency and the volume dependence has been assumed to be the same for all the vibrations in each group. By assuming that γ is different for these two groups, but the same within each group, it is possible to fit both Nayar's spectroscopic data and also the thermal expansion co-efficients in the range for which there are observed data. The values of the co-efficient of thermal expansion calculated from the new expression are definitely larger at high temperatures than those to be expected on the basis of Grüeisen's formula. The assumption of two different γs for the two groups of vibrations also appears *prima-facie* justifiable.

REFERENCES

Nayar, P. G. N. .. *Proc. Ind. Acad. Sci.*, 1942, **15**, 293 ; **1941, 13, 204.**

Mani, Anna Miss .. *Ibid.*, 1944, **19**, 231.

Krishnan, R. S. .. *Ibid.*, 1943, **19**, 216.

Raman, Sir C. V. .. *Ibid.*, 1943, **18**, 237.

Bhagavantam, S. .. *Ibid.*, 1943, **18**, 251.

Chelam, E. V. .. *Ibid.*, 1943, **18**, 334.

Dayal, Bisheshwar .. *Ibid.*, 1944, **19**, 224.

Pitzer, K. S. .. *Jour. Chem. Phys.*, 1938, **6**, 68.

Magnus and Hodler .. *Ann. der Phy.*, 1926, **80**, 808.

Grüneisen .. *Ibid.*, 1912, **39**, 257.

Adams .. *Journ. Wash. Acad. Sci.*, 1921, **11**, 45.

Williamson .. *Journ. Franklin Inst.*, 1922, 193, 41.

Fajans .. *Ber. der Dent. Chem. Ges.*, 1920, **53**, 643; **1922, 55, 2826.**

Gruneisen (*a*) .. *Handbuch der Physik.*, 1926, **10**, 41.

——————— (*b*) .. *Ibid.*, 1926, **10**, 41.

——————— (*c*) .. *Ibid.*, 1926, **10**, 42, table 12.

——————— (*d*) .. *Ibid.*, 1926, **10**, 20.

Slater (*a*) .. *Introduction to Chem. Physics*, p. 219.

——————— (*b*) .. *Ibid.*, p. 238.

——————— (*c*) .. *Ibid.*, p. 452.

Mott and Jones .. *Properties of Metals and Alloys*, p. 20.

A NEW DERIVATION OF THE DARWIN-PRINS FORMULA OF X-RAY REFLECTION

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1. Introduction

Darwin (1914) and Prins (1930) have investigated the intensity of reflection of X-rays by crystal planes, and have derived formulæ for the variation of intensity with the angle of incidence. The special case of a non-absorbing crystal was studied by Darwin, who found that the reflection is total over a small range of angles of incidence, outside which it falls away rapidly. Prins has extended Darwin's formulæ to an absorbing crystal. In essence the method is identical in both cases; it depends on the formation of a set of difference equations, and the solution of these for the case when the number of planes in the crystal is infinite. An excellent resume of the Darwin-Prins analysis is given in the book, " X-rays in Theory and Experiment," pp. 365 to 391, by Compton and Allison (hereafter referred to as C and A), whose notation we shall follow in this paper, on account of their compact nature.

An alternative method would be to solve the equations for the case when the number of planes is finite and then to extend the results for the infinite crystal. This procedure is more instructive in that it shows the manner in which the principal maximum is built up. In fact, it is found, as will be shown later, that, outside the region of perfect reflection indicated by Darwin's theory, the curve is not smooth as shown by his, but that there are an infinite number of maxima and minima, which, however, are so close together that it will not be possible to detect them. This important feature is altogether missed in Darwin's theory.

The author has actually considered such a finite stratification in an earlier paper (1942). There, a most general case of a periodic stratification was considered, in which the variation in the properties of the medium was supposed to occur periodically, the nature of this variation being unspecified. The theory can easily be applied to crystal planes, and then it can be extended to the case of a crystal of infinite depth. This is done in this paper, and the results obtained are substantially the same as those of Darwin and Prins.

It is however found that Darwin's theory leads to a different formula from that in the present paper for the region outside that of perfect reflection, which obviously arises from the failure of his theory to take cognisance of the fluctuations of intensity which occur in this region. Incidentally, it is found that a certain assumption made by Darwin and Prins is not altogether justified. The present method is free from any such, and is consequently more rigorous.

2. *General Formulæ*

Suppose that we have a medium consisting of n stratifications, and that a beam of electromagnetic radiation is incident on it. Let T_1 be the amplitude of the incident beam at the beginning of the first stratification. It is evident that there will be a large number of multiple reflections, and consequently there will be two streams of energy in the medium, one building up the transmitted beam, and the other the reflected beam. Let T_1, R_1; T_2, R_2; ....; T_{n+1} represent the electric vectors in the two streams at the beginning of the first, second, etc., stratification. If now we denote by r and t the complex reflection and transmission coefficients of a single stratification, on which the radiation is incident at the angle concerned, then the following difference equations are obtained:

$$R_s = rT_s + tR_{s+1}; \quad T_s = tT_{s-1} + rR_s \tag{1}$$

Eliminating the R's and the T's successively from these,

$$T_{s-1} = yT_s - T_{s+1}; \quad R_{s-1} = yR_s - R_{s+1} \tag{2}$$

where $y = (1 + t^2 - r^2)/t$. These can be solved by making use of the condition that $R_{n+1} = 0$. One obtains in this way

$$R_1/T_{n+1} = (r/t) \cdot f_n(y); \quad T_1/T_{n+1} = f_n(y)/t - f_{n-1}(y) \tag{3}$$

where
$$f_n(y) = y^{n-1} - \frac{(n-2)}{(1)!} y^{n-3} + \frac{(n-4)(n-3)}{(2)!} y^{n-5} - \ldots\ldots \tag{4}$$

The series appearing as $f_n(y)$ can be summed up by putting $y = 2\cosh\beta$, and comes out as $= \sinh n\beta/\sinh\beta$ (Jolley, 1925). Also, making the substitution

$$\frac{r}{\sinh\beta} = \frac{t}{\sinh\alpha} = \frac{1}{K}$$

where K can be evaluated to be equal to $\sinh(\alpha + \beta)$ from the relation $\cosh\beta = (1 + t^2 - r^2)/2t$, one finally obtains,

$$\frac{R_1}{\sinh n\beta} = \frac{T_{n+1}}{\sinh\alpha} = \frac{T_1}{\sinh(\alpha + n\beta)} \tag{5}$$

where $\cosh\beta = (1 + t^2 - r^2)/2t$ and $\cosh\alpha = (1 - t^2 + r^2)/2r$ (6)

From (5), the reflecting power, R, of the stratified medium is given by

$$\frac{1}{R} = \left|\frac{T_1}{R_1}\right|^2 = |\cosh \alpha + \sinh \alpha \coth n\beta|^2 \qquad (7)$$

This is our fundamental equation, from which the intensity of the reflected beam can be calculated by substituting the values of α and β. It may be noted that, in general, both α and β are complex.

3. *Derivation of the Formulæ for an Absorbing Crystal*

In order to determine the values of α and β, we must know those of r and t. For these, we make use of the relations, first derived by Darwin and reproduced in C and A, pp. 365 to 376. If we take the boundary between adjacent stratifications as the planes midway between the atomic planes, it is easy to show from the above formulæ in C and A that

$$r = -ise^{-ik\delta/2} \text{ and } t = (1 - i\sigma)e^{-ik\delta/2} \qquad (8)$$

where s and σ are two constants depending on the nature of the planes, $k = 2\pi/\lambda$, and $\delta = 2d \sin \psi$, d being the distance between the planes, ψ the angle of incidence, and λ the wavelength of the X-rays. The quantities σ and s are given by

$$(\lambda \sin \psi/2\pi d)\,\sigma = \mu_c - 1 = -(\delta + i\beta) \qquad (9)$$

where μ_c is the complex refractive index of the crystal, whose real and imaginary parts are, respectively, $(1 - \delta)$ and β, and

$$s = f(2\psi, k)\,\sigma/f(0, k),$$

so that $(\lambda \sin \psi/2\pi d)\,s = -(\delta + i\beta)$. $f(2\psi, k)/f(0, k) = -(\Delta + ib)$ (10)

where $f(2\psi, k)$ and $f(0, k)$ are quantities proportional to the atomic structure factors for angles 2ψ and zero. (C and A, p. 376). In the above expressions, σ and s are to be taken as small.

Now, we are interested in the phenomena that occur near about the Bragg angle, for which $k\delta/2 \simeq n\pi$. Putting $k\delta/2 = n\pi + \xi$, where ξ is small, $\exp(-ik\delta/2) = (-1)^n \exp(-i\xi)$, and

$$r = (-1)^{n+1} is\, e^{-i\xi}, \text{ and } t = (-1)^n (1 - i\sigma)e^{-i\xi} \qquad (11)$$

From these, treating σ, s and ξ as small quantities, one obtains

$$\cosh \alpha = (-1)^{n+1}(\sigma + \xi)/s; \quad \cosh \beta = (-1)^n \{2 + s^2 - (\sigma + \xi)^2\}/2 \qquad (12)$$

In the general case of an absorbing crystal, both σ and s are complex quantities, so that both $\cosh \alpha$ and $\cosh \beta$, and hence α and β, are complex. Now, the reflecting power of a finite stratification is given by (7). In order to determine the same for an infinite one, we must put $n \to \infty$ in the right

hand side of (7). If β is complex, it is easily shown that $\underset{n\to\infty}{\mathrm{Lt}} \coth n\beta = 1$, so that for an infinite stratification,

$$\underset{n\to\infty}{\mathrm{Lt}} \frac{T_1}{R_1} = \cosh \alpha + \sinh \alpha \tag{13}$$

Now, from (12), $\cosh \alpha = (-1)^{m+1} (\sigma + \xi)/s$, so that $\sinh \alpha = \pm\sqrt{(\sigma + \xi)^2 - s^2}/s$, and

$$\underset{n\to\infty}{\mathrm{Lt}} \frac{R_1}{T_1} = -s/\{(-1)^m (\sigma + \xi) \pm \sqrt{(\sigma + \xi)^2 - s^2}\} \tag{14}$$

This is identical with the Eq. (6·42) in C and A, p. 380, except for the factor $(-1)^m$ before $(\sigma + \xi)$ in our above expression. The difference is easily explained, for the amplitudes are measured at points on the planes in the derivation in C and A, while in ours, the reference point is at a distance $d/2$ above the first plane. It is obvious that this would produce a phase change of $\exp(-ik\delta/2)$, which, for small values of ξ, reduces to $(-1)^m$ exactly the factor by which the two expressions differ. It is thus seen that Prins's formula can be derived easily from our general formulæ by substituting the appropriate values of r and t.

4. *The Case of a Non-Absorbing Crystal*

We now consider the case of a non-absorbing crystal. Here, β and b in Eqns. (13) and (14) are equal to zero, so that both σ and s are real. Hence, both $\cosh \alpha$ and $\cosh \beta$ are real, and two separate cases have to be considered, *viz.*,

case (i) $|\cosh \alpha| < 1$, for which $|\cosh \beta| > 1$, and

case (ii) $|\cosh \alpha| > 1$, and $|\cosh \beta| < 1$.

From (12), $|\cosh \alpha| = 1$, if $(\sigma + \xi) = \pm s$, or $\xi = -\sigma \pm s$.

Hence, if $-\sigma - s < \xi < -\sigma + s$, case (i) is operative, so that $\sinh^2 \alpha$ is $-ve$ and $\sinh^2 \beta$ is $+ve$. If one writes $\alpha = \alpha_1 + i\alpha_2$, and $\beta = \beta_1 + i\beta_2$, then

$$\frac{1}{R} = |\cos \alpha_2 + i \sin \alpha_2 \coth n\beta_1|^2 = 1 + \frac{\sin^2 \alpha_2}{\sinh^2 n\beta_1} \tag{15}$$

Therefore, as n is increased, the intensity corresponding to any value of ξ within this range steadily increases. When $n \to \infty$, $\sinh^2 n\beta_1 \to \infty$, and $R \to 1$, *i.e., the reflection is total throughout the whole range of values of* ξ *from* $-\sigma - s$ *to* $-\sigma + s$ *for an infinite stratification.* This region may be called the principal maximum, and its width is given by $\Delta\xi = 2s$.

Outside this range, case (ii) is operative, so that $\sinh^2\alpha$ is $+ve$ and $\sinh^2\beta$ $-$ ve. Hence, in this case,

$$1/R = 1 + \sinh^2\alpha_1/\sin^2 n\beta_2 \tag{16}$$

In this region, a number of maxima and minima occur corresponding to $n\beta_2 = s\pi + 1/2$ and $s\pi$ respectively. These may be referred to as subsidiary maxima, and they all lie evidently on the curve $R = \operatorname{sech}^2\alpha_1$. When the number n increases, the intensity corresponding to any value of ξ in this region does not tend to a limit, but only undergoes fluctuations. Also, the subsidiary maxima approach closer and closer together. When n actually tends to infinity, the subsidiary maxima would be so close together, and the fluctuations in the intensity would be so rapid, that they would not be detected. The observed intensity would only be an average over a cycle of changes, and the observed value of R would be given by

$$R_{obs} = \frac{1}{\pi}\int_{\theta}^{\theta+\pi} R\, d(n\beta_2) = \frac{1}{\pi}\int_{\theta}^{\theta+\pi} \frac{\sin^2 n\beta_2}{\sin^2 n\beta_2 + \sinh^2\alpha_1}\, d(n\beta_2) \tag{17}$$

The integration can be carried out, and leads to the remarkably simple result that

$$R_{obs} = 1 - |\tanh\alpha_1| \tag{18}$$

Now, the boundary between the two regions is obviously given by $\sinh\alpha_1 = 0$, for which $\tanh\alpha_1 = 0$ and $R_{obs} = 1$. Thus, in the second region, R_{obs} starts from unity and quickly drops down as the value of ξ is taken farther and farther away from a principal maximum. These features are all very similar to those predicted by Darwin's theory. In fact, the reflection curve is not symmetric about $\xi = 0$, but $\xi = -\sigma$, or, $k\,\delta/2 = m\pi - \sigma$. The value of this shift caused by refraction, as also of the width of the region of perfect reflection can be obtained in angular dimensions. If θ_0 be the Bragg angle defined by $k\,\delta\,2 = kd\,\sin\theta_0 = m\pi$, and if θ be the angle of incidence corresponding to the centre of the diffraction pattern, then

$$\theta - \theta_0 = -\sigma/kd\cos\theta_0 = \delta\sec\theta_0\operatorname{cosec}\theta_0 \tag{19}$$

Also, if the angular width of perfect reflection be $\Delta\psi$, then

$$\Delta\psi = s/kd\cos\theta_0 = \Delta\sec\theta_0\operatorname{cosec}\theta_0 \tag{20}$$

Both these are identical with the relations derived in C and A, pp. 388 and 389.

5. *A Note on Darwin's Method of Solving the Difference Equations*

In the preceding section, it was shown that the reflection coefficient in the region outside the principal maximum is $R = 1 - |\tanh\alpha_1|$. Darwin's

formula, put in terms of our symbols, gives $\mathbf{R} = e^{-|2\alpha_1|}$ in the same region. The disagreement needs an explanation. It arises from a certain assumption made by Darwin in solving the difference equations. In terms of our symbols Darwin puts $\mathbf{T}_2/\mathbf{T}_1 = x$, and obtains $\mathbf{R}_1/\mathbf{T}_1$ in the form

$$\mathbf{R}_1/\mathbf{T}_1 = (r^2 - t^2 + tx)/r \tag{21}$$

The problem thus reduces to the evaluation of x, and for this, *Darwin makes the assumption that* $\mathbf{T}_{s+1} = \mathbf{T}_1 x^s$. By substituting this in (2), he gets

$$x = e^{\pm\beta} = \cosh\beta \pm \sinh\beta \text{ and } \mathbf{R}_1/\mathbf{T}_1 = \cosh\alpha \pm \sinh\alpha. \tag{22}$$

For the absorbing crystal, the same procedure is followed (C and A, p. 378).

It is to be noted that such an *a priori* assumption cannot be justified, since we are actually trying to find the values of the quantities $\mathbf{T}_s$ and $\mathbf{R}_s$. A more serious objection to this assumption lies in the fact that it leads to an internal contradiction in the theory. Taking the case where it disagrees with the present theory, the value of x here is $\exp(\pm i\beta_2)$, so that $|x| = 1$. Hence, $|\mathbf{T}_{s+1}| = |\mathbf{T}_1|$, so that $\lim_{s\to\infty} |\mathbf{T}_s| = |\mathbf{T}_1|$. Thus the transmitted intensity is equal to the incident intensity and *the reflection must be zero.* However, by substituting the value of x in (21), Darwin actually gets $\mathbf{R} = |\cosh\alpha \pm \sinh\alpha|^2 = \exp(\pm 2\alpha_1)$. Thus proceeding in two different ways from the same assumption, one gets different results, so that the assumption itself cannot be correct.

In fact, by making use of the method of the present paper, it can be proved that the assumption holds asymptotically for the first few planes (*i.e.*, for small values of s) in Prins's case, and in the region of perfect reflection in Darwin's case. In other words, the value of x as defined by the equation $x = \mathbf{T}_2/\mathbf{T}_1$ is actually equal to $\exp(\pm\beta)$ in these cases. However, the assumption is not generally true, and is invalid in the region outside the principal maximum for a non-absorbing crystal. Details are not given for want of space.

In conclusion, I wish to express my thanks to Prof. Sir C. V. Raman for the many helpful discussions I had with him during the investigation.

Summary

In this paper is described a new derivation of the formulæ for the reflection of X-rays by perfect crystals, which forms an alternative approach to the problem to that adopted by Darwin and Prins. It consists in obtaining a solution of the difference equations which occur in the problem for a crystal containing a finite number (n) of laminations. The case of a crystal

of infinite depth is obtained from this by proceeding to the limit when $n \to \infty$. The formulæ thus obtained are identical with those of Prins for an absorbing crystal, while for a non-absorbing crystal, the width of the region of perfect reflection is in agreement with Darwin's value. However, there is a difference in the formulæ for the variation of intensity with angle outside this region. This has been shown to be due to an assumption made by Darwin which is not altogether justifiable.

REFERENCES

1. Compton, A. H., and Allison, S. K. — *X-Rays in Theory and Experiment*, MacMillan, 1935, 365–91.
2. Darwin, C. G. .. *Phil. Mag.*, 1914, **27**, 315, 675.
3. Jolley, L. B. W. .. *Summation of Series*, 1925, 70.
4. Prins, J. A. .. *Zeits. f. Phys.*, 1930, **63**, 477.
5. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, A, 1942, **16**, 366.

SYNTHETICAL EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS, PART IV

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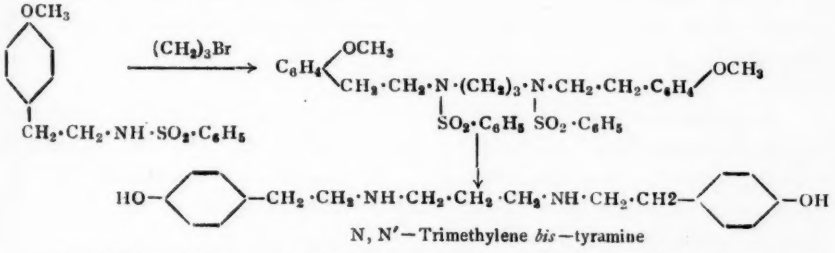
An earlier paper[1] described attempts to synthesise 9-β-aminoethyl-9: 10-dihydro-phenanthridine and a series of possible sympathomimetics derived from some carbocyclic ring systems. The latter had the repeating pressor active, atom-patterns, Ar.C.C.N.—as features of their molecular architectures and, on the basis of von Braun's conception of the mode of action of the intensely sympathomimetic methyl amino hydrindene[2], were entitled to consideration as β-phenylethylamines many times over. The present communication is concerned with attempts to synthesise further 9-β-amino ethyl-9: 10-dihydro-phenanthridine and N,N′-trimethylane *bis*-tyramine which also comes under the same category.

The scheme for the synthesis of the β-aminoethyl phenanthridine derivative could not be pursued owing to failure at the cyclisation stage of cyanacetamido diphenyl to 9-cyanomethyl phenathridine, a necessary intermediate. However, success was encountered in the scheme for the synthesis of the trimethylene *bis*-tyramine. 4-Methoxy phenyl ethylamine[3] was transformed in good yield to its N-benzenesulphonyl derivative[4]; the potassium salt of the latter gave with trimethylene bromide the corresponding alkali insoluble di-amide, which on hydrolysis, furnished the desired N,N′-trimethylene *bis*-tyramine.



N, N′—Trimethylene *bis*—tyramine

N,N′-Trimethylene *bis*-tyamine has recently been subjected by Capt. K. Venkatachalam of the Madras Medical College to preliminary biological tests in respect of its pressor activity and compared to tyramine in the spinal cat. The tests, so far conducted, reveal that while its intensity of action

is nearly equal to that of tyramine, trimethyle ıe *bis*-tyramine is superior to the standard sympathomimetic in the matter of its duration of action.

Experimental

2-*Cyanoacetamido diphenyl.*—A mixture of 2-amino diphenyl (4 g), and ethyl cyanoacetate (2·8 g.) was heated under reflux at 200–10° for 2 hours and cooled; the solid (2·5 g.) which separated was washed with dilute hydrochloric acid followed by water and crystallised from water. It was obtained as colourless needles, m.p. 126° (Found: N, 11·3. $C_{15}H_{12}ON_2$ requires N, 11·9 per cent.)

N,N′-Trimethylene bis-*tyramine hydrochloride.* The postasium salt of N-benzenesulphonyl tyramine-methyl ether was prepared *in situ* by adding the calculated quantity of potassium to a hot solution of the benzene sulphonamide (7 g.) in xylene (15 c.c.) Trimethylene bromide (2·4 g.) was then added and the mixture refluxed for 4 hours. The reaction mixture, after pouring into water and steam distillation to remove xylene completely, furnished the trimethylene diamide. The crude product was freed from the unreacted starting amide by washing successively with dilute alkali and water. The purified diamide was then heated with concentrated hydrochloric acid (10 c.c.) in a sealed tube at 160-170° for 6 hours so as to obtain hydrochloride of N,N′-trimethylene *bis*-tyramine.

The crude, dark coloured product of the pressure reaction was dissolved in absolute alcohol and fractionally precipitated with anhydrous ether, the first oily portions being rejected. The partly purified hydrochloride (1·4 g.) then recrystallised from alcohol-ether in colourless needles, m.p. 149°. (Found: N, 7·8; Cl, 18·6. $C_{19}H_{26}O_2N_2$, 2 HCl requires N, 7·2; Cl, 19·0 per cent.)

I am thankful to Professor P. C. Guha, D.Sc., F.N.I., for his kind interest in this investigation and to the Government of Madras for a Reserch Scholarship.

Summary

In continuation of an earlier line of work, synthesis has been effected of N,N′-trimethylene *bis*-tyramine which fulfils the requisite structural specifications for sympathomimecity. The results of subjecting this to preliminary biological tests in respect of its pressor action in the spinal cat are also indicated.

REFERENCES

1. Rajagopalan .. *Proc. Ind. Acad. Sci.*, 1941, **14**, 126.
2. von Braun *et al.* .. *Ber.*, 1916, **49**, 2645; 1917, **50**, 63.
3. Callow, Gulland and Haworth *J. Chem. Soc.*, 1929, 1444.
4. Walpole .. *Ibid.*, 1910, **97**, 946.

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